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# TECHNICAL MEMORANDUM

## MOBILE TAGA SURVEY

## AMBIENT CHLORINE

## BCM TECHNOLOGIES LIMITED

## AMHERSTBURG

MAY, 1986

ARB-130-86-AQM

SEPTEMBER, 1986

Ontario
Ministry of the Environment

E. PICHÉ, Director
Air Resources Branch

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- prepared for -

The Southwestern Region
Ontario Ministry of the Environment

- prepared by -

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September, 1986

## Executive Summary

As requested by the Southwestern Region, the mobile TAGA unit of the Air Resources Branch performed an air monitoring survey in Amherstburg, Ontario during the weeks of May 12 and 19, 1986. The survey objective was to determine the ambient levels of chlorine ($Cl_2$) downwind of BCM Technologies Limited which is a manufacturer of sodium chlorate ($NaClO_3$).

A total of 23 half-hour average concentrations for ambient chlorine were acquired over the survey period. The highest half-hour average for chlorine was 65 ug/m$^3$, recorded 50 metres downwind of BCM. At distances greater than 200 metres from BCM, chlorine was rarely detected above analytical detection limits of 0.3 ug/m$^3$. The Ministry standard for chlorine is 300 ug/m$^3$ for a half-hour average. The Ministry standard was not exceeded.

It is noteworthy that chlorine odours were only detected in the immediate vicinity of BCM property. Also, with the exception of chlorine, no other contaminants were detected downwind of BCM.

## Acknowledgements

The author gratefully acknowledges the dedication of Messrs. Andy Ng and David Cook of the Air Resources Branch in the operation of the mobile TAGA unit during the BCM survey.

## 1.0 Introduction

In response to a request by the Southwestern Region the TAGA unit of the Ministry's Air Resources Branch conducted a mobile air monitoring survey in Amherstburg during May, 1986. The purpose of the survey was to determine the ambient concentrations of gaseous chlorine ($Cl_2$) in the vicinity of BCM Technologies Limited located at 99 Thomas Road.

The survey request was initiated by the observation of damage to vegetation near BCM, and odour complaints. BCM produces sodium chlorate ($NaClO_3$) via the electrolysis of brine solution. Chlorine gas is produced during the manufacturing of $NaClO_3$. Thus, in May 1986 the TAGA unit was deployed to Amherstburg to investigate the BCM's chlorine contribution to the local air shed. Our findings of a two week study are reported here.

## 2.0 The Mobile TAGA and Survey Strategy

The mobile TAGA system represents the state-of-the-art in ambient air analyses. It is a completely self-contained mobile laboratory capable of monitoring a variety of organic and inorganic pollutants at ultra trace levels in the real-time. Past applications include chlorine monitoring at pulp and paper mills and during the Mississauga train derailment.

The TAGA, or Trace Atmospheric Gas Analyzer, is a specialized quadrupole mass spectrometer with a non-conventional sample inlet system and atmospheric-pressure ion source. Ambient air is sampled continuously at a high flow rate (100 l/min) directly into the ionization chamber, where contaminants are selectively ionized and mass analyzed in a matter of seconds. This unique system is especially applicable to real-time monitoring while in motion, allowing for the tracking of pollutant plumes to their source of origin.

Numerous classes of chemicals are detectable by the TAGA system including the alcohols, acids, amines, amides, aromatics, aldehydes, ketones, esters, phenols, mercaptans, sulfides, PCBs and halides. The detection limits for these chemical classes range from 0.1 to 100 ug/m$^3$ depending on the chemical and the air sample matrix.

Meteorological instrumentation has been installed in the mobile TAGA unit. Local wind speed, wind direction and ambient temperature are recorded at a height of 10 metres during the acquisition of all air quality data.

## 2.1 Chlorine Monitoring Technique

Trace levels of ambient chlorine are readily observable by the TAGA system. In TAGA mass spectrometry chlorine produces negative ions at m/z values of 70, 72, 74 corresponding to the following ionic species: ($^{35}$Cl . $^{35}$Cl)$^-$; ($^{37}$Cl . $^{35}$Cl)$^-$; and ($^{37}$Cl . $^{37}$Cl)$^-$ respectively. Owing to the natural isotope abundance of $^{35}$Cl/$^{37}$Cl (i.e. 3/1) the theoretical ratio of ion intensities for masses 70, 72, 74 are 9:6:1. Thus mass spectrometry is an ideal technique for the unequivocal detection and quantitation of chlorine. Furthermore, the exceptional sensitivity of the TAGA systems affords real-time measurements of chlorine at levels as low as 0.3 ug/m$^3$.

Calibration of the TAGA is accomplished by admitting known concentrations of chlorine from a pressurized gas bottle containing 50.9 ppm chlorine in ultra pure nitrogen. Flow control is facilitated by a standard ball rotameter pre-calibrated by the bubble metering method. The response of the TAGA to chlorine is practically linear over a concentration range expanding two orders of magnitude. Correlation coefficients better than 0.999 have been observed for 5 point calibrations over the concentration range of 3 to 300 ug/m$^3$ (approximately 1 to 100 ppb). The relative standard deviation for 10 consecutive measurements at the 100 ug/m$^3$ level is no greater than 3%. The detection limit for chlorine is typically 0.3 ug/m$^3$ as determined

by the TAGA technique. (Detection limits are defined as 3 times the standard deviation of the background signal divided by the sensitivity of the slope of the response curve.)

## 2.2 Survey Strategy

Basically, the survey strategy was to position the mobile TAGA unit directly downwind of BCM and acquire instantaneous concentrations of ambient chlorine. Monitoring locations were selected based on the following criteria in order of importance:

1) prevailing wind direction;
2) roads network and accessibility;
3) plume tracking results;
4) presence of odours.

Every 30 seconds wind speeds and directions at a height of 10 metres were updated and displayed by the on-board data acquisition system. The survey scientist monitored the changes in local meteorological conditions and, if necessary, re-located the mobile unit. It should be noted, however, that the lack of public roadways in the immediate vicinity of BCM limited the choices for monitoring sites. Given the topography of the area the desired wind directions for monitoring were NNW to NNE or SSE to SSW. It was necessary, therefore, to wait for the "right" winds so that meaningful data could be ascertained.

The presence of chlorine-like odours was not always a prerequisite for monitoring since it was entirely possible that ambient chlorine levels were below the odour threshold limits, particularly for monitoring sites in excess of 1 kilometre from BCM.

Plume tracking refers to the real-time acquisition of the instantaneous concentrations of chlorine while the TAGA is mobile. Provided the winds are steady and the chlorine levels are above background levels,

plume tracking can immediately reveal the source of a unique pollutant. In this study, however, the meteorological conditions were not always satisfactory and thus plume tracking was of limited value.

Once a sampling site had been selected instantaneous levels of chlorine were recorded every 10 seconds for a period of at least 30 minutes. The half-hour average concentration of chlorine was obtained by simply calculating the arithmetic mean of 181 measurements acquired over a 30 minute period. Several half-hour averages for chlorine were acquired at various distances downwind of BCM.

Prior to any downwind measurements the background levels of chlorine were determined by monitoring the target masses (70, 72, 74) directly upwind of BCM. The background or upwind abundances were then subtracted from the downwind readings to yield the contribution of BCM to the ambient chlorine levels. The TAGA was calibrated at least once daily, usually at the upwind locations. It is noteworthy that for all sites upwind of BCM chlorine was not detected above the detection limit of 0.3 $ug/m^3$.

## 3.0 Results and Discussion

Mobile air monitoring for gaseous chlorine was conducted on May 13, 14, 15, 16, 20, 21 and 22, 1986 in the immediate vicinity of BCM Technologies Limited, Amherstburg. A total of 23 half-hour average concentrations for chlorine are reported in Table 1, together with the meteorological data, an estimate of the source to receptor distance, and relevant comments regarding the sampling periods. Peak concentrations refer to the single highest instantaneous levels of chlorine recorded during the corresponding 30 minute sampling periods. Chlorine levels were determined during various times of the day and night, at several distances from the source, and under diverse meteorological conditions.

Monitoring locations were confined to the four closest concessions surrounding BCM: Thomas Road, Alma Street, Fox Road, and Texas Road. Fourteen (14) of the 23 half-hour samples were acquired on Thomas Road within roughly 50 metres of BCM. As discussed below, the highest levels of chlorine were observed at this location. See Figure 1 for the approximate locations of all monitoring sites.

Odours characteristic of chlorine were only evident at locations within 200 metres of BCM. Furthermore, the chlorine odours were generally faint and quite transient.

As shown in Table 1 the half-hour average concentration for chlorine downwind of BCM ranged from not detectable (i.e. less than 0.3 ug/m$^3$) to 65 ug/m$^3$. The highest and most persistent levels of chlorine were recorded at locations B and D during the afternoon of May 14, 1986. During this sampling period the concentrations were fairly consistent at the 50 to 65 ug/m$^3$ level. The peak instantaneous concentrations were in the hundreds of ug/m$^3$ range. Note that chlorine levels were approximately two orders of magnitude lower at site E, roughly 1.5 kilometres downwind on Texas Road. Sampling at Site E was also performed during the afternoon of May 14.

An example of actual real-time data recorded from 14:48 to 15:18 hours on May 14 is shown in Figure 2. The large variations in the instantaneous concentrations are probably due to the variance in wind speeds and directions. Although the maximum instantaneous level of chlorine was 410 ug/m$^3$, the concentration averaged over the 30 minute monitoring period was only 65 ug/m$^3$ which is well below the Ministry standard of 300 ug/m$^3$ for a half-hour average.

On May 15 and 16 the ambient chlorine levels downwind of BCM were no greater than 30 ug/m$^3$ for a half-hour average. In fact, 4 of the 6 samples showed chlorine concentrations less than 10 ug/m$^3$.

Only traces of ambient chlorine were recorded during the second week of the survey. One exception is sample #15 (site H) when the half-hour average concentration was 7.5 ug/m³. Regardless, for most of the sampling periods on May 20, 21, 22 chlorine levels were below the analytical detection limits of 0.3 ug/m³. It must be noted, however, that the meteorological conditions during the last 3 days were less than ideal; that is, very light, variable winds with occasional rain.

Mass spectral screening of the air downwind of BCM revealed that, with the exception of chlorine, no other volatile contaminants detectable by the TAGA system were presence. This would include chlorine dioxide ($ClO_2$).

In summation, the results of a two week survey conducted in May, 1986 by the mobile TAGA unit indicated that the chlorine levels in the vicinity of BCM's chlorate plant were well below the Ministry standard of 300 ug/m³. Furthermore, chlorine odours were generally confined to the immediate area of the plant.

TABLE 1: Chlorine Concentrations (½-hr Av.) Measured in the Vicinity of BCM Technologies Limited. Mobile TAGA Survey, May 1986, Amherstburg

| Sample Number | Date | Start[1] Time | Site[2] | Approx. Distance From BCM | Met. Conditions[3] AT | WS | WD | Concentration (ug/m³) ½-hr Av. (Peak)[4] | Comments |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 13/5/86 | 14:59 | A | 1.5 km | 26 | 0-15 | W | ND (ND) | No odours |
| 2 | 14/5/86 | 14:18 | B | 50 m | 24 | 10-20 | S | 60 (370) | Chlorine odours |
| 3 | 14/5/86 | 14:48 | B | 50 m | 23 | 10-20 | S | 65 (410) | Chlorine odours |
| 4 | 14/5/86 | 15:39 | C | 200 m | 25 | 10-25 | SSE | 2.5 (25) | No odour, edge of plume(?) |
| 5 | 14/5/86 | 16:21 | D | 25 m | 25 | 10-20 | SSE | 50 (250) | Chlorine odour |
| 6 | 14/5/86 | 16:52 | D | 25 m | 26 | 5-20 | SSE | 65 (310) | Chlorine odour |
| 7 | 14/5/86 | 17:53 | E | 1.5 km | 26 | 10-20 | SSE | 2.0 (6) | No odour |
| 8 | 14/5/86 | 18:23 | E | 1.5 km | 26 | 10-20 | SSE | 0.6 (3) | No odour |
| 9 | 15/5/86 | 11:07 | F | 25 m | 24 | 10-20 | SW | 3.3 (70) | Faint odour, plume shifted |
| 10 | 15/5/86 | 11:38 | F | 25 m | 26 | 10-20 | SSW | 12 (110) | Faint odour |
| 11 | 15/5/86 | 13:03 | C | 200 m | 24 | 15-25 | S | 30 (100) | Faint odour, transient |
| 12 | 15/5/86 | 13:34 | C | 200 m | 23 | 25-35 | S | 5.2 (45) | Faint odour, transient |
| 13 | 16/5/86 | 00:08 | D | 25 m | 19 | 10-15 | SSW | 5.5 (45) | Intermittent faint odours |
| 14 | 16/5/86 | 01:03 | G | 35 m | 19 | 10-15 | S | 7.1 (30) | Intermittent very faint odours |
| 15 | 20/5/86 | 09:49 | H | 25 m | 11 | 5-7 | NNW | 7.5 (75) | Faint odour/wind shift last 12 min. |
| 16 | 20/5/86 | 10:33 | I | 300 m | 12 | 5-7 | WNW | ND (ND) | No odours, light winds |
| 17 | 20/5/86 | 11:45 | I | 300 m | 12 | 0-5 | WNW | ND (ND) | No odours, very light winds |
| 18 | 20/5/86 | 12:55 | H | 25 m | 12 | 0-5 | NW | 0.9 (15) | No odours, very light winds |
| 19 | 21/5/86 | 03:37 | H | 25 m | 10 | 5-10 | WNW | ND (ND) | No odours, rain |
| 20 | 21/5/86 | 23:44 | J | 1.5 km | 11 | 5-10 | WSW | ND (ND) | No odours |
| 21 | 22/5/86 | 02:14 | D | 25 m | 11 | 4-6 | WSW | ND (ND) | No odours, rain, light winds |
| 22 | 22/5/86 | 19:44 | K | 30 m | 12 | 0-3 | - | ND (3) | No odours, nil winds |
| 23 | 22/5/86 | 20:22 | L | 20 m | 12 | 0-3 | - | ND (10) | No odours, nil winds |

Note [1] All monitoring periods are 30 minutes.
[2] See Figure 1 for monitoring locations.
[3] AT = ambient temperature (°C); WS = range of wind speeds in km/hr; WD = predominant wind direction.
[4] (Peak) refers to single highest instantaneous concentration of chlorine during the ½-hr sampling period.

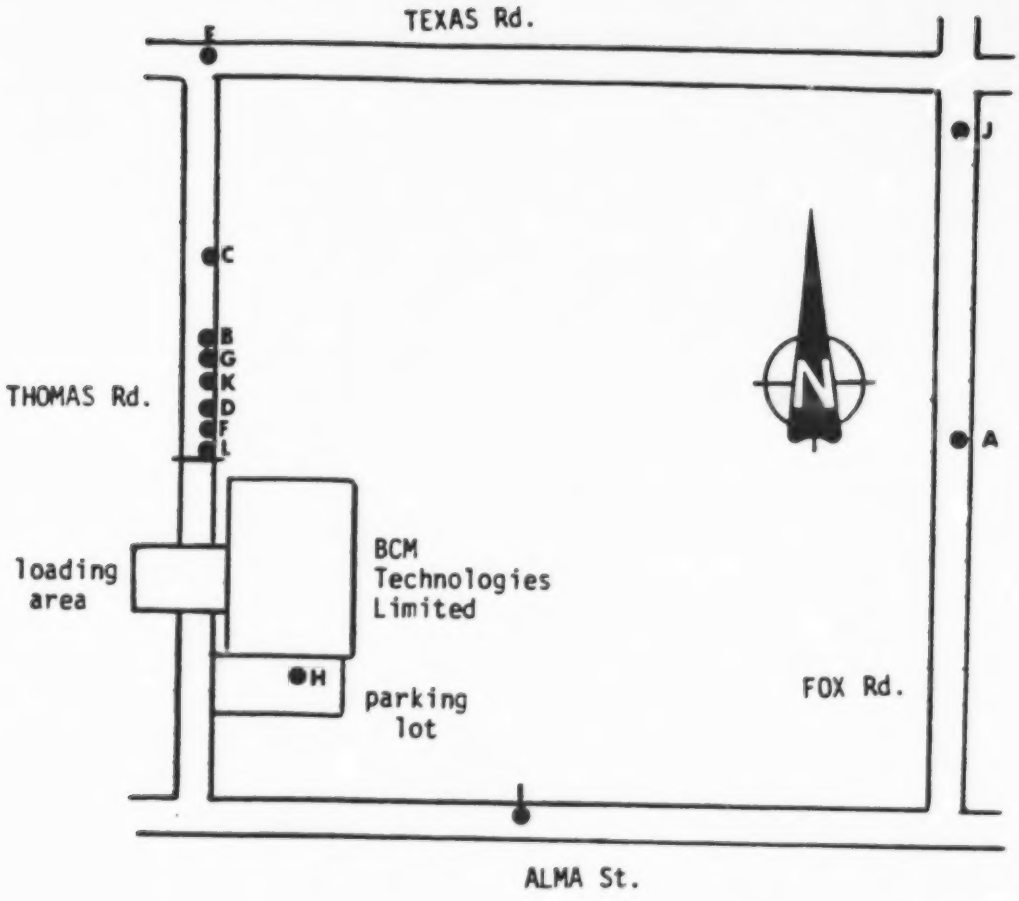


Figure 1: Map of the vicinity of BCM Technologies Limited, 99 Thomas Rd., Amherstburg showing TAGA monitoring locations. NOT TO SCALE. Distance between parallel concessions roughly 1.5 km.

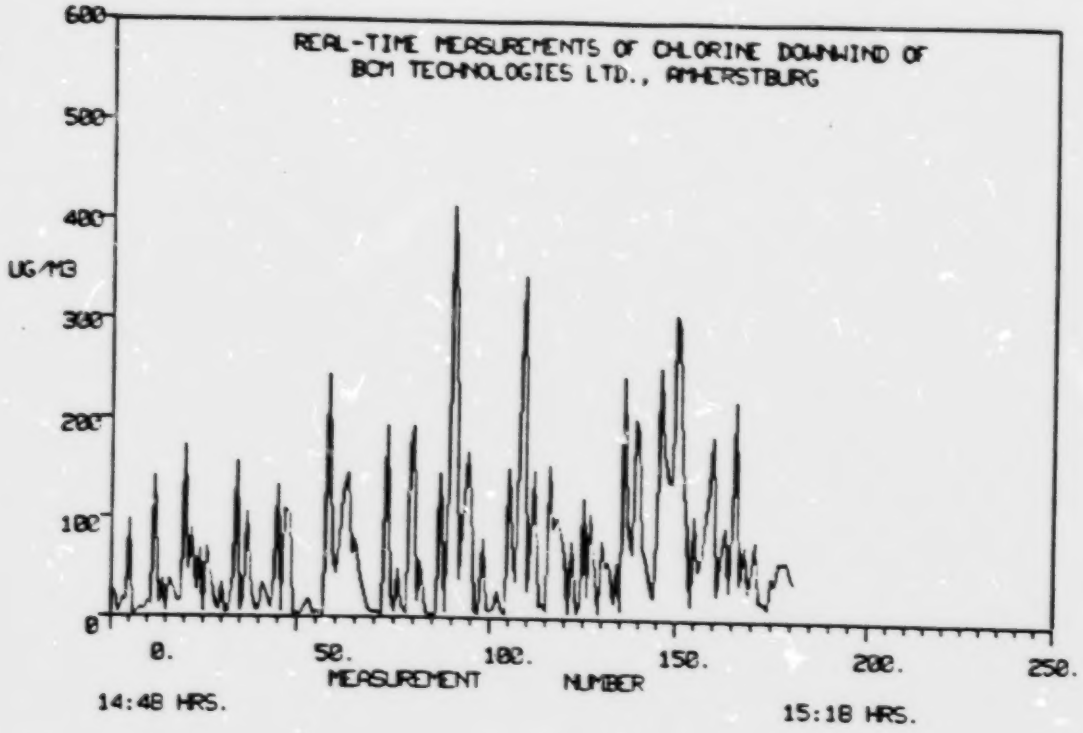


FIGURE 2. REAL-TIME MEASUREMENTS OF CL2 (SAMPLE 3)
RECORDED 14-MAY-86 14:48 - 15:18 HOURS. MONITORING
LOCATION: SITE B (THOMAS RD.) DOWNWIND OF BCM.
MEASUREMENT TECHNIQUE: MAMU #3 (MOBILE TAGA UNIT).
1/2 HR. AV. CONCENTRATION: 65 UG/M3.
PEAK (INSTANTANEOUS)LEVEL: 410 UG/M3.